The Effect of Interfacial Polysilane Coating on Heat Fusion Properties of Polypropylene

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We investigate the effect of an interfacial phenyl-methyl polysilane (PMPS) coating on the heat-fusion properties of polypropylene (PP). Application of PMPS to the heat-fusion interface of PP films increases the peeling strength such that modified films cannot be peeled off, unlike PP films without PMPS under identical conditions. Therefore, modified films can be heat-fused at a much lower temperature than neat samples. Upon addition of silicone oil of nearly the same molecular weight as PMPS to the surface of PP films, the peeling strength decreases dramatically. Field emission transmission electron microscopy results show a discontinuous heat-fusion boundary in the neat PP sample, even when the sample is completely heat-fused. However, when PMPS is applied to PP film surfaces, the boundary at the heat-fusion interface is barely observable; instead, continuous lamella crystals are observed at the interface. Viscoelastic measurements of PP films with added PMPS record an activation energy of 30.9 kJ mol⁻¹ for the molecular motion of PP in the heat-flow region, which is lower than that of neat PP (34.9 kJ mol⁻¹). This result indicates that PMPS enhances the molecular motion of PP in the molten state.

Key Words: Polysilane / Polypropylene / Heat fusion / Mechanical properties / Morphology

1. INTRODUCTION

Heat fusion is a widely employed adhesion process for polymer materials, in particular for polyolefin such as polyethylene (PE) and polypropylene (PP). It is so ubiquitous because of its low cost, ease of processing and low environmental impact. If the heat-fusion process is completed inadequately, problems such as content leakage may occur. Therefore, a technique that increases the effectiveness of the heat-fusion process is required. Additionally, polymer films can wrinkle and shrink in response to external heating during the heat-fusion process because the temperature is much higher than the glass-transition temperature or melting temperature of the polymer. Consequently, lower temperatures and shorter exposure times are also required to improve the heat-fusion process.

It has been found that a certain kind of polysilane (PSi) material can be compatibilized with polyolefin¹⁻². PSi can also improve the heat-fusion properties of PE³, lower the heat-molten viscosity of ultra-high-molecular-weight polyethylene (UHMWPE)⁴, and lower the glass-transition temperature (Tg) of amorphous cyclo-olefins⁵. PSi materials are remarkable polymers with backbones composed of Si–Si bonds. These organosilicon compounds also have functional organic side groups, and as a result they possess both organic and inorganic properties⁶⁻¹¹. The organic properties of PSi materials are what make them compatible with polyolefin, while the Si–Si backbone grants these polymers photo- and electronic-properties similar to those of semi-conductive silicones, such as photoconductivity¹²,¹³, photo-reactive properties¹⁴⁻¹⁶, high heat-resistance¹⁷,¹⁸, and non-linear optical properties¹⁹⁻²¹. The mechanisms by which the interfacial PSi coating improves the heat-fusion properties of PE films and the nature of the interaction between polyolefin and PSi at the heat-fusion boundary remain unclear, however. In this paper, we report the effects of an interfacial PSi coating on the heat-fusion properties of PP, as well as studying its effects on the molecular motion of PP.
2. EXPERIMENTAL

2.1 Materials

Isotactic PP was purchased from Prime Polymer Co. Ltd., Japan (F113G, MFR = 3.0 g/10 min at 230 °C). A polysilane material, phenyl-methyl polysilane (PMPS), with molecular weight Mw = 700 g mol\(^{-1}\) was provided by Osaka Gas Chemical Co. Ltd., Japan. Additionally, to compare the difference between a Si–Si and Si–O backbone, we used a silicone oil (Si-oil) with phenyl and methyl groups in its structure (Shin-Etsu Chemical Co. Ltd., KF-54, Si-oil: Mw = 2820 g mol\(^{-1}\)). The chemical structures of PMPS and Si-oil are shown in Fig. 1.

2.2 Preparation of test specimens

PP film samples were prepared by hot-pressing under the following conditions: temperature was 180 °C, soaking time was 5 min, and hot-pressing pressure was 10 MPa. After hot-pressing, all film samples were quenched in hot water (100 °C).

As a peel test specimen was T-shaped film, a heat-fused film was prepared by hot-pressing two PP films with the heat-fused area of 10 mm in length and 50 mm in width, using a polyimide film as a spacer (The spacer part of polyimide film cannot be heat-fused between the PP films). 1.0 mg cm\(^{-2}\) of either PMPS or Si-oil was added to the surface of the PP films. Then they were hot-pressed by using a Heat-seal Tester (Tester Sangyo Co. Ltd., Japan; TP-701-B), and the heat fusion treatment was performed at a temperature of 160 °C, a pressure of 0.05 MPa, and a sealing time of 40 to 120 seconds.

The blend samples, PP and PMPS (PP/PMPS), PP and Silicone-oil (PP/Si-oil), were prepared using a kneading machine with twin-rotor (Labo Plastomill 50M, Toyo Seiki Seisaku-sho Co. Ltd., Japan) at 200 °C for 10 min.

2.3 Characterization

Peel tests

Peel tests on PP films were carried out using a tensile tester (EZ-Test, Shimadzu Co., Ltd., Japan) under tensile mode at ambient temperature according to the standard JIS K 6854-3 (ISO 11339). A peel test specimen was prepared by cutting a heat-fused specimen in 2.2 into a length of 10 mm and a width of 5 mm, and the length of the gripping part of the chuck was 10 mm as described in Fig. 2. Tensile head speed in the peel test was set at 10 mm min\(^{-1}\) and the initial chuck distance was 10 mm. Peel tests were carried out with at least five repetitions for each sample. Peeling energy can be calculated from the area under the stress–strain curves of the heat-fused PP films in the peel test.

FE-TEM observation

Field emission transmission electron microscopy (FE-TEM) observations were carried out at the heat-fused boundary of PP films on a JEM-2100F, JEOL Co., Ltd., Japan. To study the distribution of Si atoms derived from polysilane (PMPS) in the blended PP films, energy dispersive x-ray spectroscopy (EDS) line profile measurements on scanning transmission electron microscopy high angle annular dark field (STEM-HAADF) observations were carried out, for which the samples were stained with RuO4 prior to the measurement.

Differential scanning calorimetry (DSC) measurement

DSC measurement was carried out over a temperature range of 30 to 200 °C at a heating rate of 10 °C min\(^{-1}\) in a N\(_2\) atmosphere, using a DSC 60 A (Shimadzu Co., Ltd, Japan) instrument. The degree of crystallinity (Xc) was obtained by using Eq. (1),

![Fig. 1 Chemical structure of (a) polysilane (PMPS) and (b) silicone oil (Si-oil).](image1)

![Fig. 2 Peel test specimen shape and peel test condition.](image2)
\[
X_c = \frac{\Delta H_m}{\Delta H_m^{\text{cry}} \times \phi}
\]

(1)

where \(\Delta H_m\) and \(\Delta H_m^{\text{cry}}\) indicate the enthalpy of fusion for the PP samples and perfect crystallites of PP (209 J g\(^{-1}\)), and \(\phi\) is the weight fraction of PP in the PP samples.

**Dynamic mechanical measurement (DMA)**

DMA measurement was carried out using a dynamic viscoelastometer (Rheogel E-4000, UBM Co., Ltd., Japan) under tensile mode with an initial chuck distance of 20 mm at a frequency of 30 Hz and a heating rate of 2 °C min\(^{-1}\) over a temperature range of −150 °C to 150 °C. Test specimens were 0.4 mm in thickness, 3 mm in width, and 30 mm in length.

**Rheological measurement**

Rheological measurement was carried out using a dynamic rheometer (CVO-100, Bohlin Co., Ltd., Japan) under a controlled stress mode with parallel plates of 25 mm diameter at a frequency of 0.01 to 20 Hz over a temperature range of 180 °C to 240 °C in N\(_2\). From the shift factor, \(a_T\), the activation energy of PP molecules at the melt condition could be calculated using Eq (2),

\[
\ln a_T = \frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)
\]

(2)

where \(\Delta H\), \(T\) and \(R\) indicate the activation energy, temperature \((T_0:\) reference temperature) and gas constant, respectively.

**3. RESULTS AND DISCUSSION**

**3.1 Heat-fusion properties and morphological observations of PP films**

Figure 3 shows the peeling test results for pristine PP (indicated by a black bar), PP with PMPS (white bar), and PP with Si-oil (gray bar) at a heat-treatment temperature of 160 °C. As can be seen in this figure, the peeling energy could be determined readily for the PP films with PMPS; the peeling energy increased with heat-fusion time, until finally at 120 sec, the films were heat-fused completely (NP: not peelable). In the NP sample, peeling did not occur on the heat fusion surface, and rupture occurred in areas other than the fused area as indicated in Fig. 3. It should be noted that when the heat-fused sample is heat-fused completely, peeling energy cannot be measured and its value becomes infinite. In Fig. 3, NP sample is also shown together, and the upper limit of the vertical axis is shown as 3000 mJ cm\(^{-2}\). After heat-treating for 60 sec, the peeling energy of the pristine PP films was much lower than that of the PP films with PMPS. Additionally, the peeling energy of neat PP films increased for longer heat-fusion times; however, the values remained lower than those of PP with PMPS, which had been heat-fused for the same time. Moreover, the pristine PP films were not heat-fused completely at 120 sec, which was the time it took for complete heat-fusion of PP with PMPS. It took 300 sec for the pristine PP films to be heat-fused completely at that temperature. Conversely, the peeling energies of all PP films with Si-oil heat-treated at the same temperature and for the same time were much lower than those of both the pristine and PMPS-treated PP films. This result demonstrates that Si-oil hinders the heat-fusion process of PP films.

Figure 4 shows the FE-TEM observation results for (a) pristine PP films, (b) PP films with PMPS, and (c) PP films with Si-oil. All of the films were heat-treated at 160 °C for 300 sec. Under these conditions both the pristine PP films and the PP films with PMPS were heat-fused completely \(i.e.\) not peelable, but the PP films with Si-oil were not heat-fused, and they could be peeled off easily. As shown in these images, the film boundary is clearly visible for the PP with Si-oil and the pristine PP, even though peel testing confirmed that the pristine PP films were heat-fused. In contrast, the film boundary of the PP with PMPS was barely observable, and the continuous lamellar structure of PP was instead observed where the heat-fusion boundary was thought to be (as indicated by the thick arrows in Fig. 3 (b)). From these results, we deduce that the primary role of PMPS is not to modify the adhesion properties, but to act as an accelerator for the molecular motions or re-crystallization properties of PP.

Figure 5 shows the FE-TEM result of the neat PP, and the blend samples of PP/PMPS (5 wt%) and PP/Si-oil (5 wt%). When comparing the neat PP (Fig. 4 (a)) and PP/PMPS blend sample (Fig. 4 (b)), there is no obvious difference but it was found that PMPS was distributed homogeneously in the PP matrix, because no phase separation or
segregation of PMPS could be observed at all. Conversely, in the case of the PP/Si-oil blend sample, phase separation of the Si-oil and the PP matrix was readily observed, as is visible in Fig. 4 (c). These results therefore demonstrate that PMPS can be dispersed homogeneously in a PP matrix, unlike Si-oil. Then, to confirm the existence of Si atoms derived from PMPS in the PP/PMPS blend sample, STEM-HAADF measurements were carried out; the results are shown in Fig. 6 (a) and (b). Figure 6 (a) showed the line profile of Ru and Si and the sample was stained using RuO₄ prior to observation. Therefore, the amorphous regions are visible as “white areas” in the image, owing to the large amount of Ru, in the meanwhile, the crystalline regions are visible as “black areas” owing to the far lower Ru content. In Fig. 6 (a), Si atoms originating from PMPS can mainly be observed in the same regions in which there are large amounts of Ru. Figure 6 (b) shows the Element mapping images of Ru and Si, indicating the Ru atoms are red dots and Si atoms green dots. Although there is a difference in shading depending on places, as a whole, it can be seen that a large amount of Si element is present in the vicinity of the site where Ru element exists, which means that PMPS is mainly located in the amorphous

![Fig. 4](image-url) TEM results for heat-fused PP/PP films at 160 °C for 300 sec under 0.05 MPa: (a) neat PP, (b) with PMPS (1.0 mg/cm²) and (c) with Silicone oil (1.0 mg/cm²).

![Fig. 5](image-url) FE-TEM results for PP films: (a) Neat PP, (b) PP/PMPS (5 wt%) and (c) PP/Si-oil (5 wt%).

![Fig. 6](image-url) HAADF-STEM and line profile analysis image of PP/PMPS (5 wt%).

![Fig. 5](image-url) FE-TEM results for PP films: (a) Neat PP, (b) PP/PMPS (5 wt%) and (c) PP/Si-oil (5 wt%).
region of PP. From the above mentioned results, we conclude that PMPS is homogeneously distributed in the amorphous regions of the PP matrix and that no phase separation or segregation of PMPS occurred at all. The reason for this is not yet clear to us, but PMPS reportedly has a good infinity with PP as well as with other polyolefins, including PE and cyclo-polyolefin\textsuperscript{1, 6, 7}.

### 3.2 Molecular motion and rheological properties of PP

Figure 7 shows the DMA results for (a) storage modulus ($E'$), loss modulus ($E''$), and (b) tan$\delta$, of neat PP and PP with PMPS (5 wt% and 10 wt%). It was found that the onset temperature marking the decline of $E'$ and $E''$ shifted lower for PP with PMPS. Moreover, in the $\beta$ relaxation region, which corresponds to the molecular motion of PP in the amorphous region (around 10 °C), the intensity of tan$\delta$ increases with increasing PMPS content and, at the same time, the peak temperature gradually shifts to lower values. These results indicate that PP with PMPS can be softened at lower temperatures than neat PP, because the molecular motion of PP in the amorphous region is enhanced by adding PMPS.

Figure 8 shows the DSC results of neat PP, PP with PMPS (5 wt%), and PP with PMPS (10 wt%). As can be seen in this figure, the melting temperature of the samples decreased slightly with an increase of PMPS content, and the degree of crystallinity of the PP matrix tended to increase gradually with an increase of PMPS content: neat PP (29.4%), PP with 5 wt% PMPS (31.8%), and PP with 10 wt% PMPS (34.2%). When taking the results of both the FE-TEM and DMA measurements into consideration, we conclude that the molecular motion of PP at the amorphous region can be enhanced by adding PMPS, resulting in a decrease of the lamellar size of PP for an increasing amount of PMPS. Therefore, the melting temperature of PP decreases with an increase of PMPS content at the same time as the degree of crystallinity of PP is increased.

To estimate the molecular motion of PP at melt-flow conditions, viscoelastic measurements were carried out for neat PP, PP with PMPS (5 wt%), and PP with Si-oil (5 wt%) over the temperature range of 180 °C to 240 °C. As shown in Fig. 9, when the curves are horizontally shifted by the shift factor, $\alpha_T$, a master curve is obtained; these master curves did not change during the heating and cooling cycles. Therefore, it was found that no cross-linking reaction or degradation of the PP molecules had occurred, even after adding the PMPS or Si-oil onto the PP films. Figure 10 shows the shift factor...
Fig. 9  Variation of log $G'$ against frequency of (a) neat PP, (b) PP/PMPS (5 wt%), and (c) PP/Si-oil (5 wt%).

Fig. 10  Variation of $-\log a_T$ vs. $-(1/T - 1/T_0)$ : (a) neat PP, (b) PP/PMPS (5 wt%), and (c) PP/Si-oil (5 wt%).
against the reciprocal of temperature, $1/T$; from these graphs the activation energy of the molecular motion of PP can be obtained for each sample. The activation energy of PP/PMPS was lower than that of neat PP in the heat-flow region of PP. This result indicates that PMPS can lower the activation energy of PP molecules and can enhance the molecular motion of PP under heat-flow conditions. The activation energy of PP/Si-oil was also lower than that of the neat sample, but it was higher than that of the PP/PMPS blend. Therefore, neat PP had the highest activation energy for molecular motion, followed by PP with Si-oil; PP with PMPS had the lowest activation energy. Figure 11 shows the dynamic viscosity, $\eta'$, against the frequency of neat PP, PP with PMPS (5 wt%), and PP with Si-oil (5 wt%), all at a temperature of 180 °C. (Dynamic viscosity, $\eta'$, can be calculated by $G''/\omega$, and it is also related to Complex viscosity, $\eta^*$, as $\eta^* = \eta' + i\eta''$.) As you can see in this figure, the $\eta'$ of PP with PMPS decreases dramatically, and it was found that PP with PMPS has the lowest value of all samples at any temperature. Therefore, we conclude that PMPS can lower the dynamic viscosity of PP at any temperature.

4. CONCLUSIONS

In this paper, the effects of adding polysilane (PMPS) and silicon oil (Si-oil) on the heat-fusion properties and the molecular motion of PP were investigated and the results are summarized as follows:

(a) When adding PMPS on the surface of a PP film, it can enhance the heat-fusion properties of PP, lower the heat-fusion temperature and shorten the processing time. Si-oil, however, hindered the heat-fusion of PP films.

(b) FE-TEM images of the heat-fused films show that the film boundary can be observed clearly for the pristine PP and PP with Si-oil samples, even though the pristine PP films were heat-fused according to peel tests. However, such a film boundary was barely observable for PP with PMPS, and the continuous lamellar structure of PP can be observed at the location of the film boundary.

(c) FE-TEM images of neat PP, and PP/PMPS (5 wt%) and PP/Si-oil (5 wt%) blend samples, showed that PMPS could be dispersed homogenously in a PP matrix and was mainly located in the amorphous regions of PP. However, Si-oil underwent phase-separation with the PP matrix and thus Si-oil has a negative effect on the heat-fusion properties of the PP film.

(d) The DMA results showed that the intensity of $\tan\delta$ increased with an increase of PMPS content in the $\beta$ relaxation region, which is correlated to the molecular motion of PP in the amorphous region at around 10 °C. At the same time, the peak temperature gradually shifted to lower values as well. These results indicated that PP with PMPS can be softened at a lower temperature than neat PP, because the molecular motion of PP in the amorphous region is enhanced by adding PMPS.

(e) PMPS can enhance the molecular motion of PP in the amorphous region in solid state PP. Moreover, PMPS can lower the activation energy of the molecular motion of PP under heat-flow conditions. Although the activation energy of PP/Si-oil was lower than that of neat PP, it was higher than that of the PP/PMPS blend. Starting from the lowest value, the activation energies were: PP/PMPS (30.9 kJ mol\(^{-1}\)) < PP/Si-oil (32.9 kJ mol\(^{-1}\)) < neat PP (34.9 kJ mol\(^{-1}\)).

(f) The DSC results showed that the melting temperature of PP decreases with increasing PMPS content, while the degree of crystallinity in the PP matrix increases gradually (neat PP (29.4 %), PP with 5 wt% PMPS (31.8 %), and PP with 10 wt% PMPS (34.2 %)). From the FE-TEM and DMA measurement, we deduce that the molecular motion of PP in the amorphous region can be enhanced by adding PMPS, which also results in a decrease of the lamellar size of PP with increasing PMPS content. Therefore, the melting temperature of PP can be decreased with an increased PMPS content, while also increasing the degree of crystallinity of the PP sample.
In conclusion, PMPS that has a Si–Si backbone has the remarkable property of being able to both modify the heat-fusion properties and enhance the molecular motion of PP. However, Si-oil that has a Si–O backbone does not have such an important effect on PP. The reasons for this are not yet clear to us, but we suggest that PMPS has some kind of strong interaction with PP molecules, and as a result, the addition of PMPS in the PP matrix can cause an enhancement of the molecular motion of PP.

This study did not determine the type of interactions that exist between the polysilane and PP matrix. However, because elemental Si belongs to the carbon group in the periodic table, we believe it is possible that polysilanes with organic functional groups as side chains have a good affinity with organic materials. Further investigation is required to confirm this assumption.

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